Design Rules for Advanced Materials: Neutron Scattering and Neutron Spin-Echo

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Thanks to…

Hydrogels: Introduction

❑ Crosslinked polymer networks that can absorb as much as 99% water by volume.

❑ Are biocompatible.

❑ Widely used in applications

   - personal care, pharmaceutical, biomedical, controlled release, lab-on-chip analytics etc.

Hydrogels: Recap

❑ Hydrogels can absorb and retain as much as 99% water by volume.

❑ Can be biocompatible.

❑ Widely used in applications

    - personal care, pharmaceutical, biomedical, controlled release, lab-on-chip analytics etc.

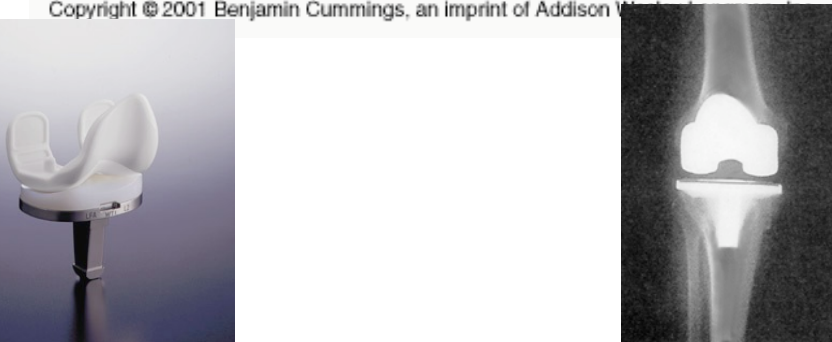❑ **But are inherently weak to sustain high mechanical loads.**
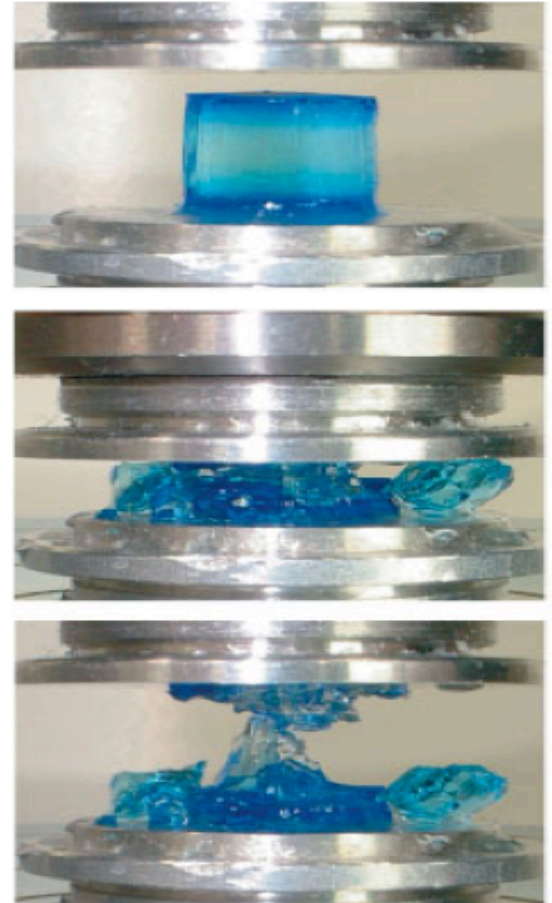
Conventional hydrogels

Grand Challenge: Synthetic Cartilage
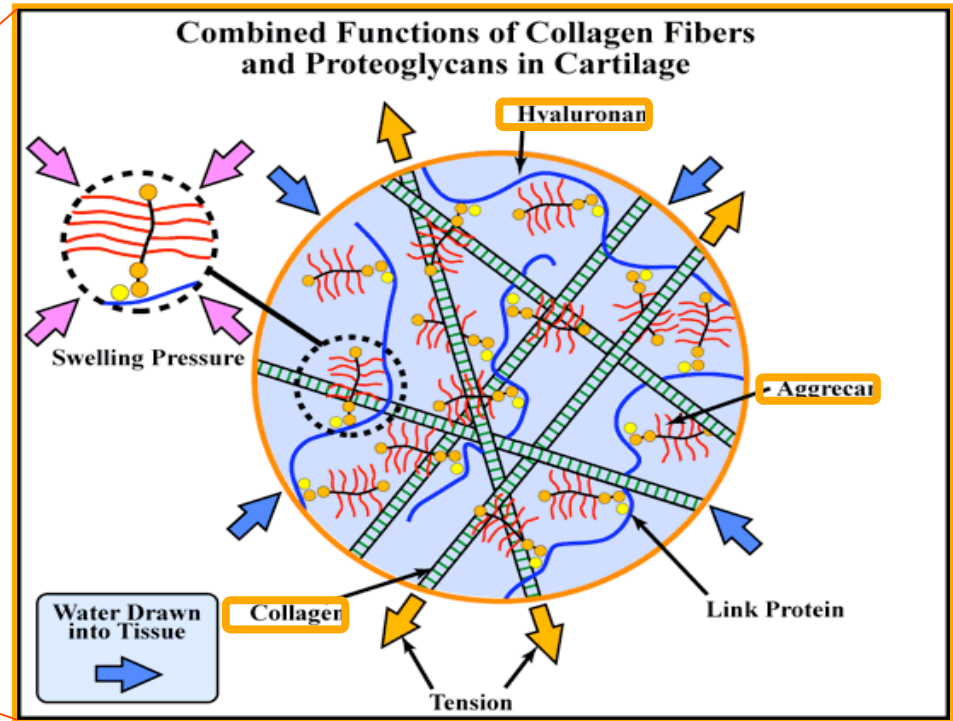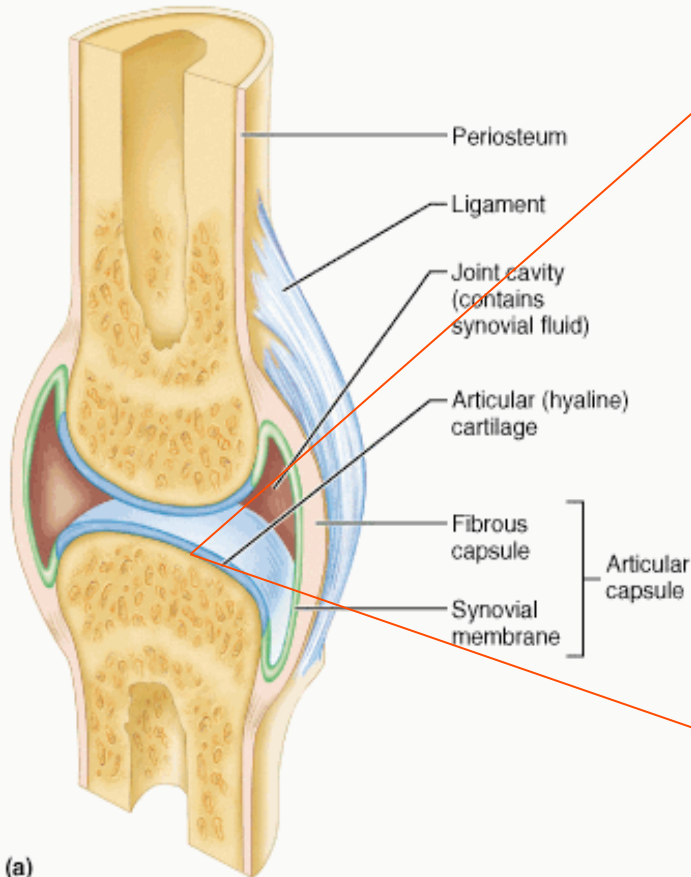
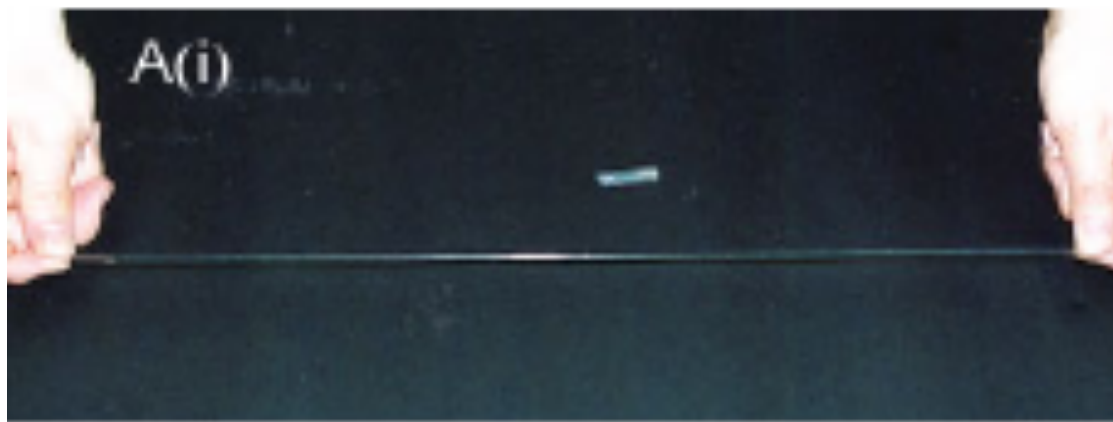Contains 80% water by vol.

TOUGH!
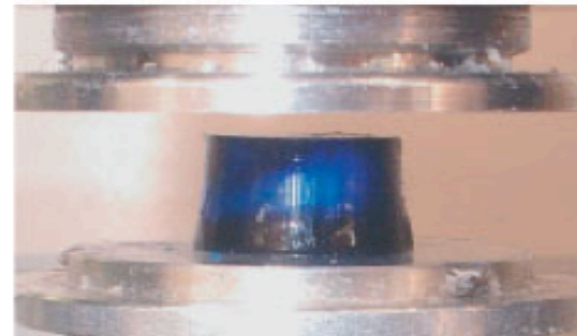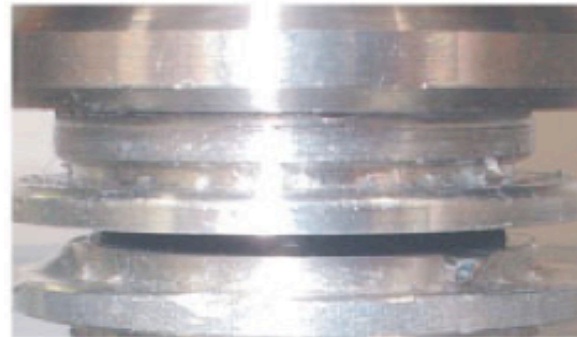
Hydrogels w/ Improved Mechanical Properties
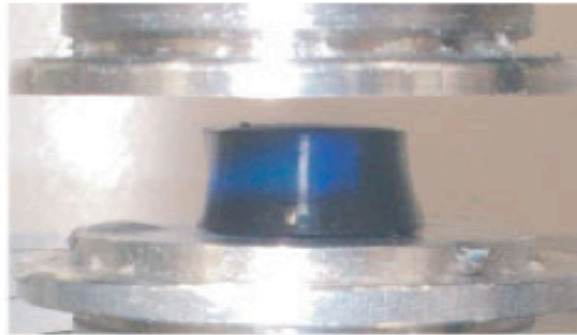
A number of approaches are explored to improve the extensibility of hydrogels: (i) polyrotoxane crosslinks,

(ii) clay nanocomposites, etc.

NONE, however, improve the toughness.
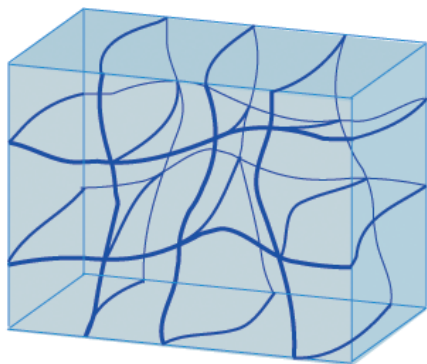
Double-Network Hydrogels (J.P. Gong *et al*., *Adv. Mater.* **2003**,*15,*1155.)
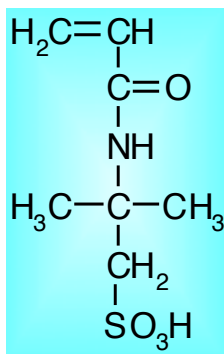

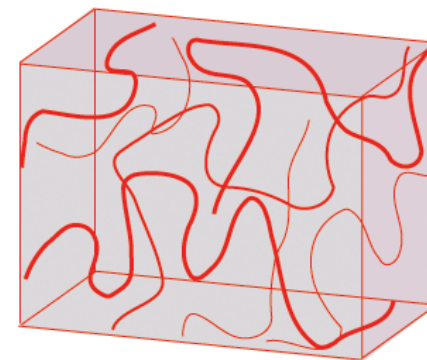Tough but elastic!

> 85% water by vol.

DN-gels

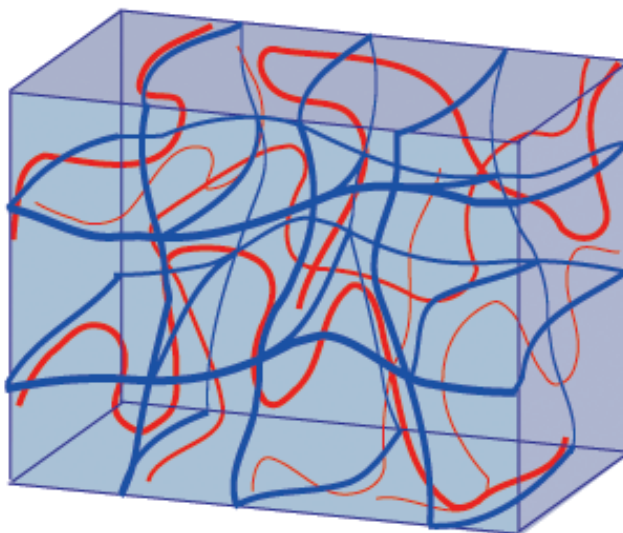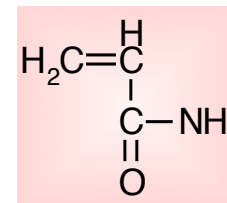1st network : PAMPS
(polyelectrolyte, rigid)

2nd network:PAAm
(neutral, soft)

$H_2C=CH$
$C=O$
NH
$H_3C-C-CH_3$
CH_2
SO_3H

2-acrylamido, 2-methyl
propane sulfonic acid (AMPS)

$H_2C=C$
H
$C-NH_2$
O

Acrylamide (AAm)

DN-gels: PAMPS/PAAm
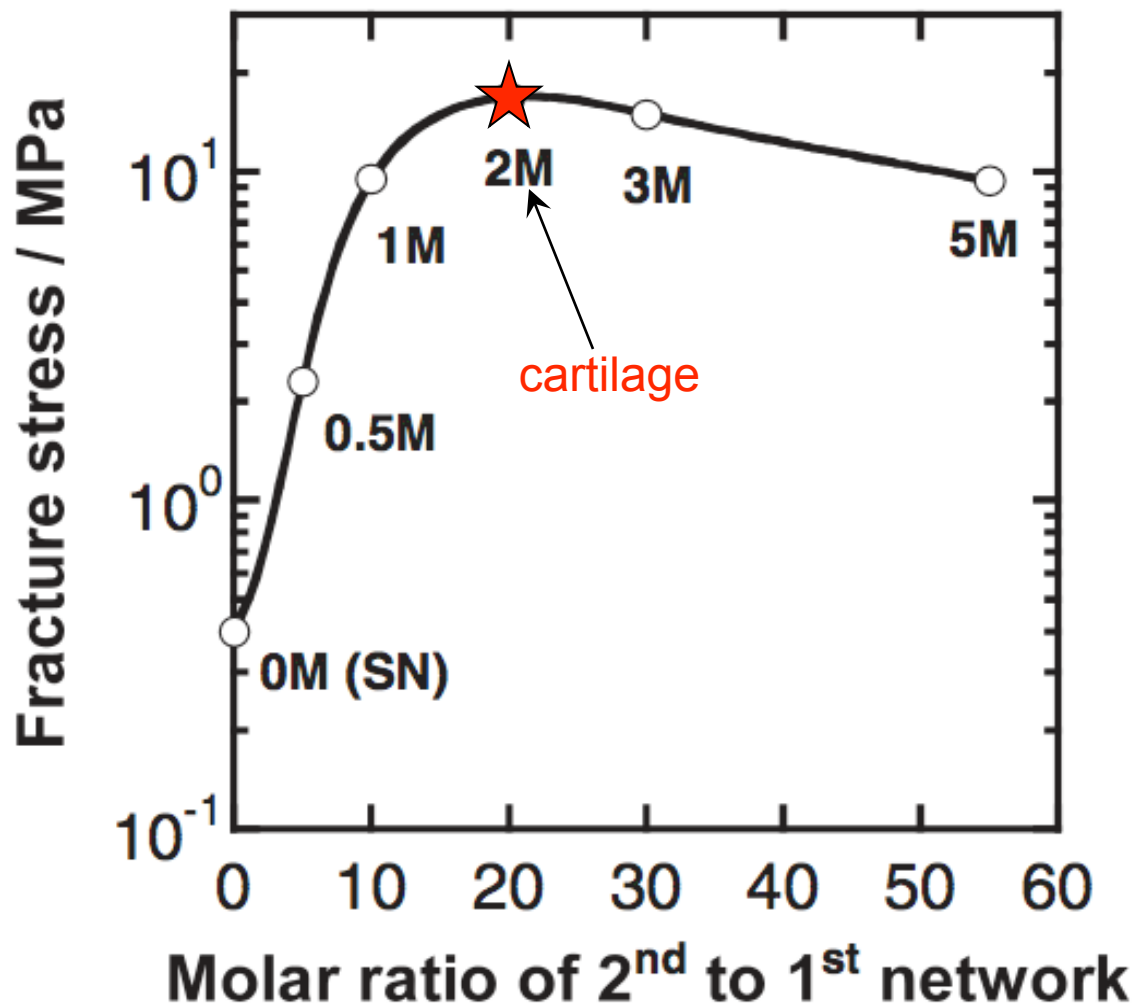
Synthetic alternative to tissue cartilage.

A fairly general approach

Table 1. Compressive properties of hydrogels at room temperature.

| First network	Second network	Water content [wt.-%]	Fracture stress σ_{max} [MPa]	Fracture strain λ_{max} [%]	$\sigma_{max}^{DN}/\sigma_{max}^{SN}$
PAMPS-1-4 [a]	–	92	0.4	41	–
	PAMPS-2.2-0.1	93	3.0	80	7.5
	PAA-1-0.1	92	2.3	75	5.8
	PAAm-2-0.1	90	17.2	92	43
PAMPS-1-8	–	98	0.006 [b]	0.13 [b]	–
	TFEA-1-0.1	52	1.6 [b]	4.9 [b]	267
PAA-1					
PAAm-1-1	–	93	0.7	98	–
	PAAm-1-0.1	92	5.4	92	7.7
P(AMPS-*co*-TFEA)-1-4	–	98	0.03	73	–
	AAm-1-0.1	93	21.0	97	700
Collagen [c]	–	93	0.26	52	–
	PDMAAm-1-0.1	87	2.9	53	11
Agarose [c]	–	96	0.02	20	–
	HEMA-2.5-0.1	66	2.4	87	120
Bacteria cellulose	–	–	–	–	–
	Gelatin	78	3.7	37	31 [d]

How do flexible polymer chains reinforce a brittle primary network?

[a] *P-x-y*: *P*, *x*, and *y* denote the abbreviated polymer name, molar monomer concentration, and the crosslinker concentration in mol-% with respect to the monomer, respectively. [b] Stretching properties. [c] Physically cross-linked gel prepared from 2 wt.-% solution. [d] Relative to gelatin SN gel.

J.P. Gong *et al.*, *Adv, Matter.* **2003**,*15*,1155.

Synergism in Tough DN-gels:

Rule of thumb in Mixtures (composites/blends/IPN):
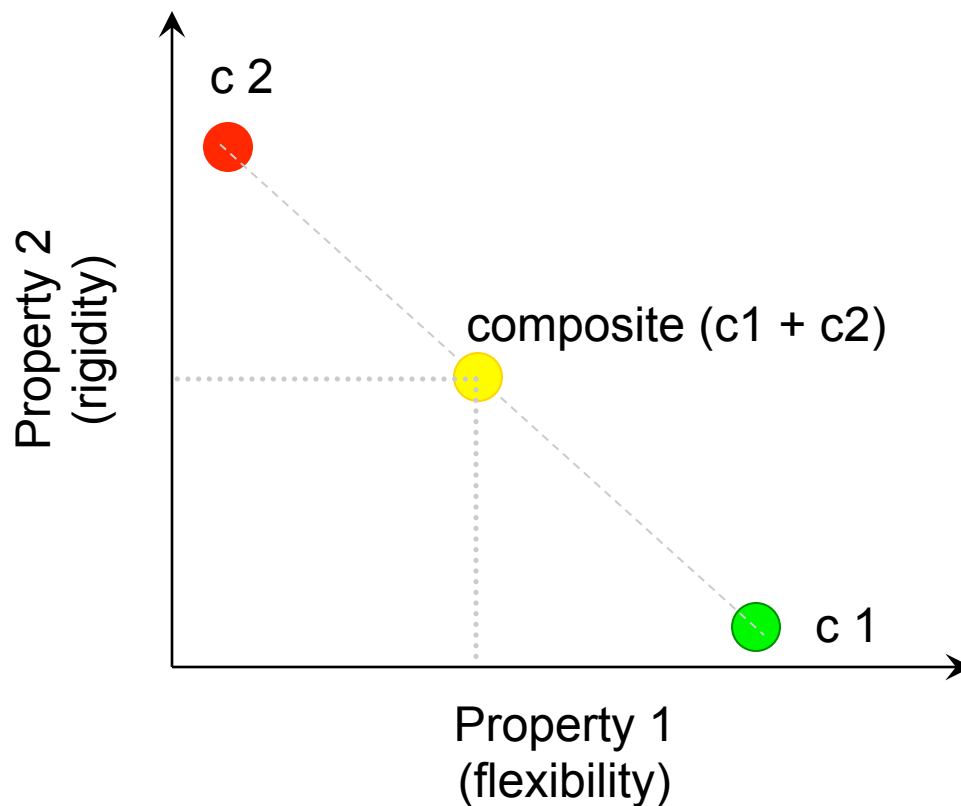
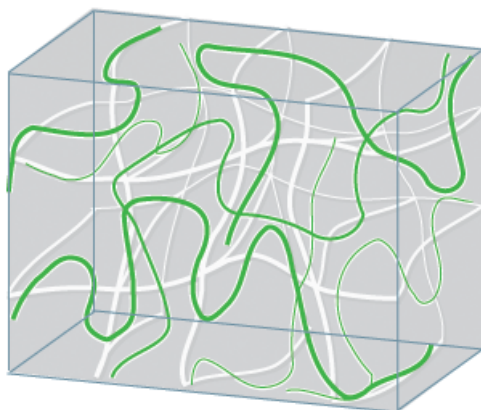**Toughness is off the chart.**

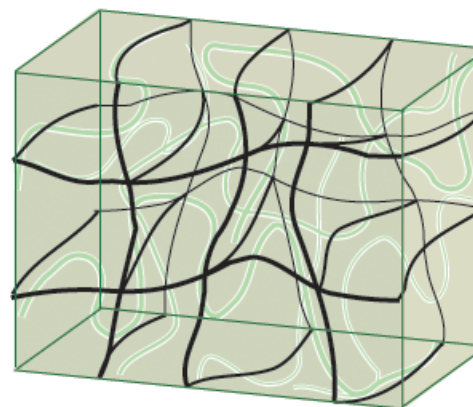# Advantage of Neutron Scattering: Contrast Variation
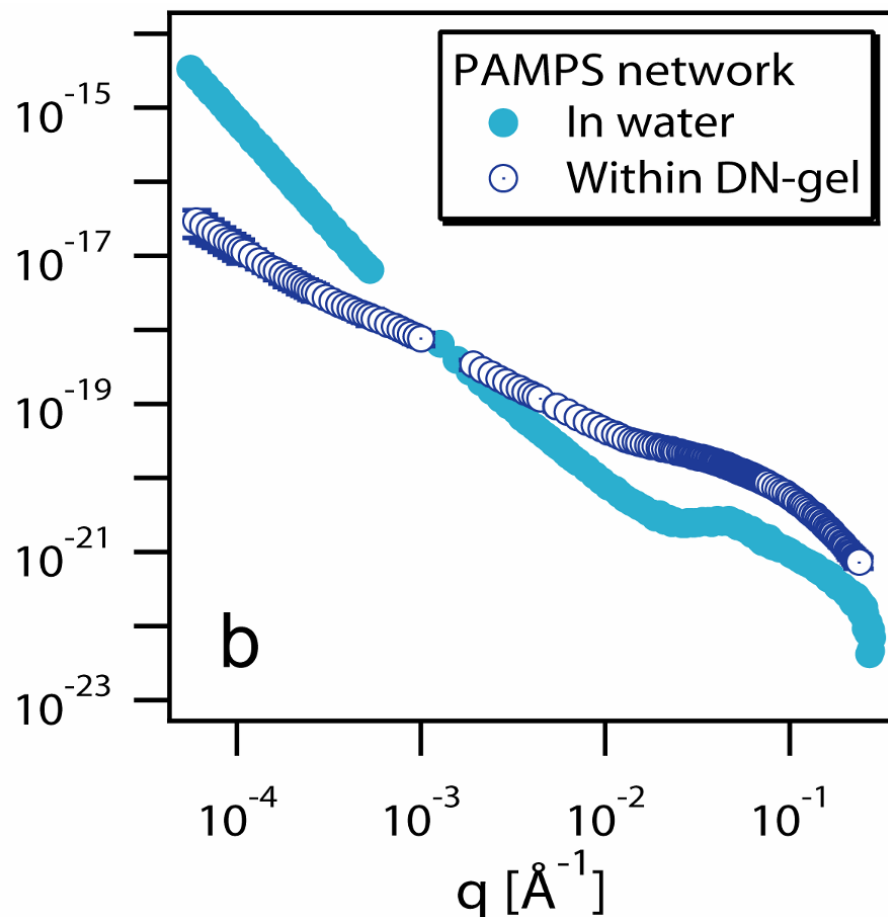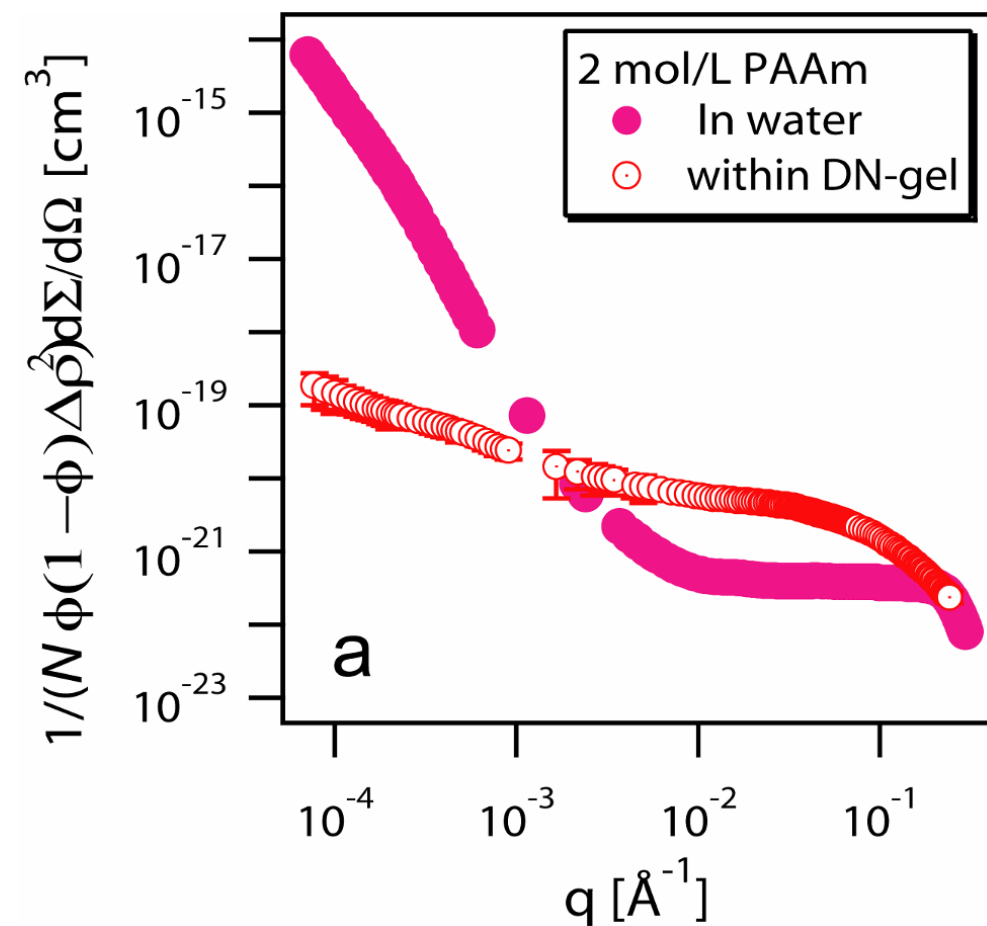
PAAm linear chains alone

PAMPS network alone

AMPS/d_3-AAm in H_2O

AMPS/d_3-AAm in D_2O/H_2O

∿	hydrogenated	▢	H_2O
∿	deuterated	▢	D_2O

$$2nm < \xi < 12\mu m$$
$$(5 \times 10^{-5}\,\overset{o}{A} < q < 0.3\,\overset{o}{A}) \quad (\xi = \frac{2\pi}{q})$$

PAMPS and PAAm: In water and in DN-gels

Tominaga, Tirumala *et al. Polymer* **2007**.
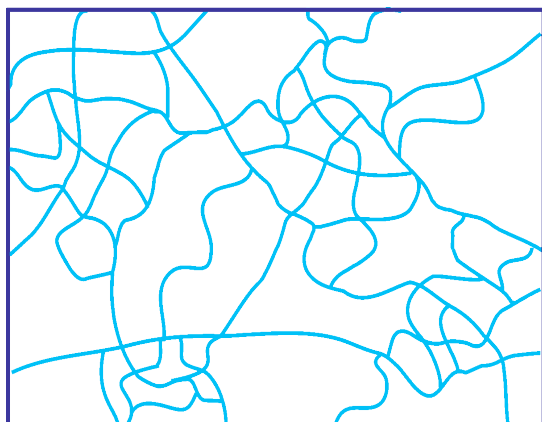
Schematic for structure of PAMPS (blue) and PAAm (red) in DN-gels
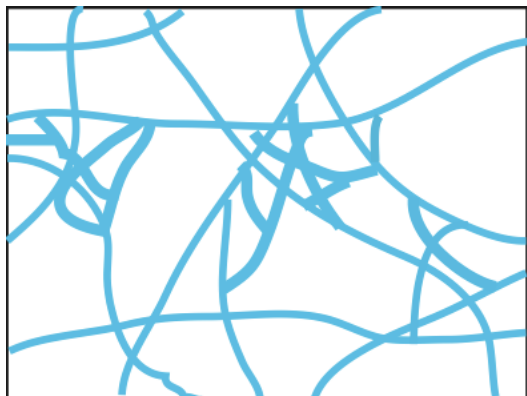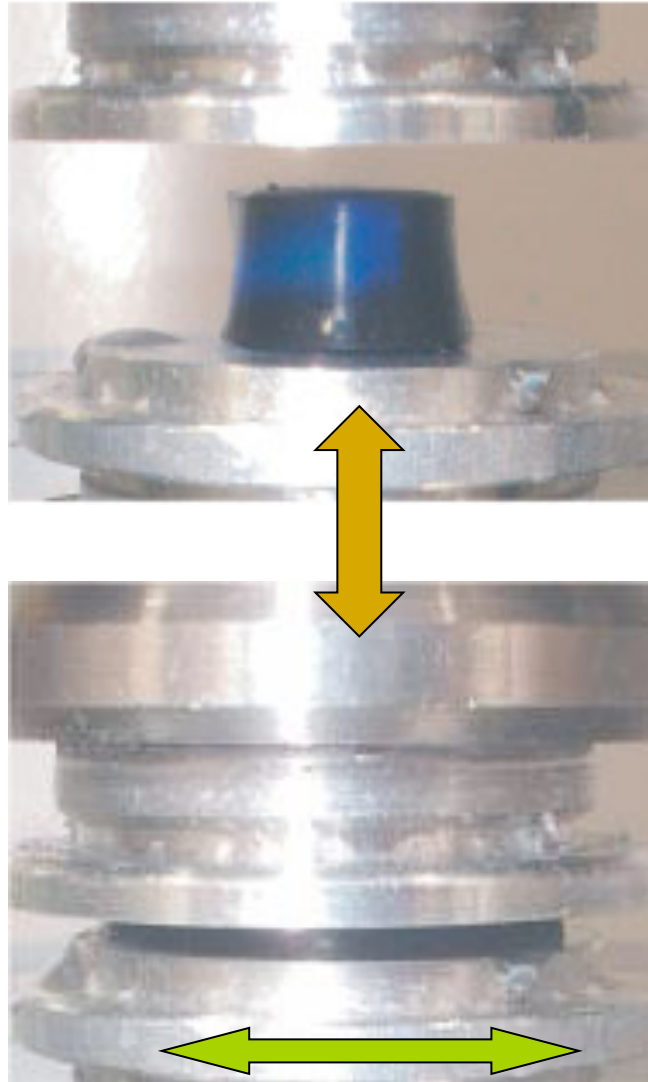

PAMPS in D_2O
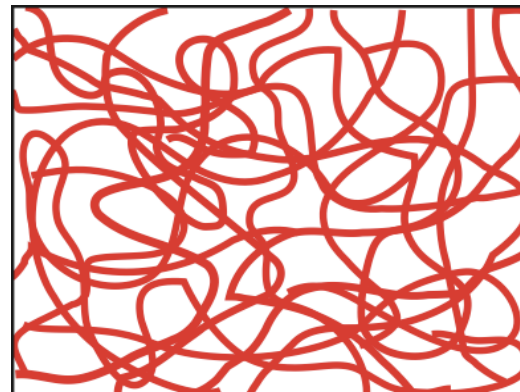
PAAm in D_2O

PAMPS in DN

PAAm in DN

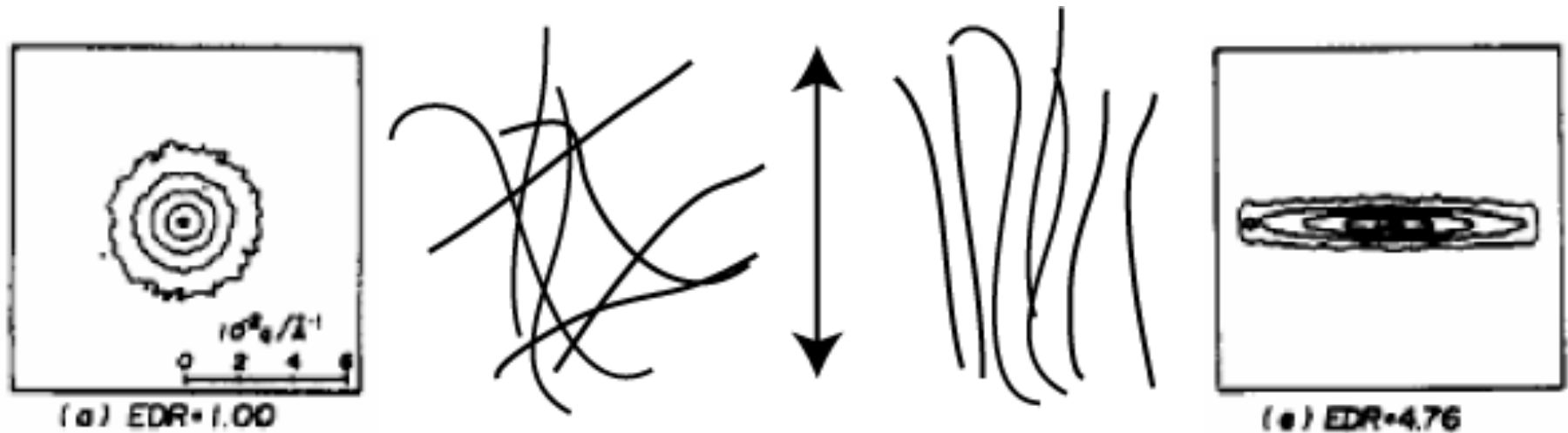**PAMPS and PAAm dissolve better in water when in presence of the other.**

Response to Compression?

Uniaxial Deformation of Neutral Polymers

Solvent-cast and uniaxially extruded poly (vinyl alcohol) films.

(a) EDR=1.00

(e) EDR=4.76

Shibayama, M.; Wu, W.-L, *et al. Macromol.*, **1990**, *23*, 1438.

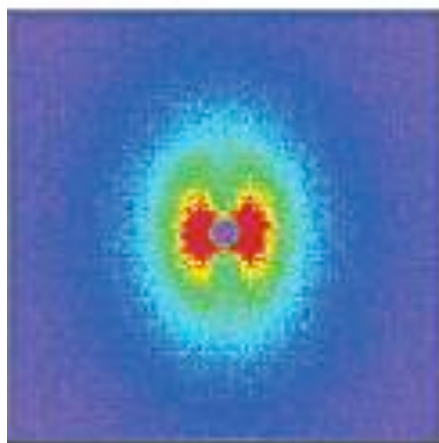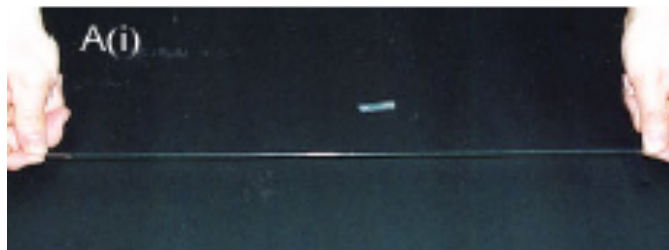Scattering Intensity lower in stretching direction: $I_\perp > I_{||}$

Affine deformation → Polymer chains readily deform along the extension axis.

Uniaxial Deformation of Extensible Gels

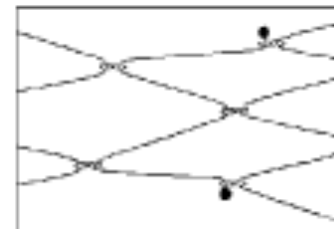Haraguchi and Takehisa, *Adv. Mater.* **2002**.

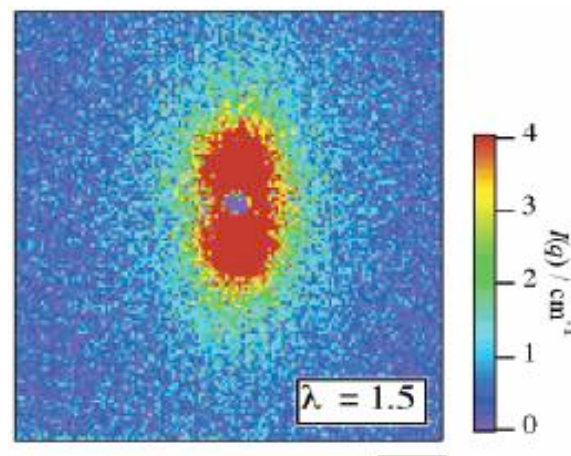Shibayama, Takehisa, Haraguchi, *Macromol.* **2005**.

Okumura and Ito, *Adv. Mater.* **2001**.

Okumura, Ito, Shibayama, *Macromol.* **2005**.
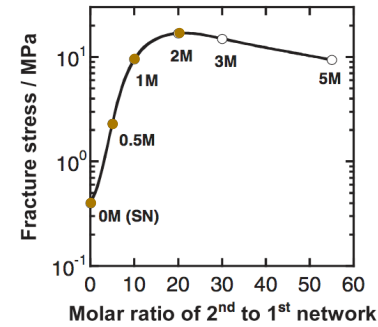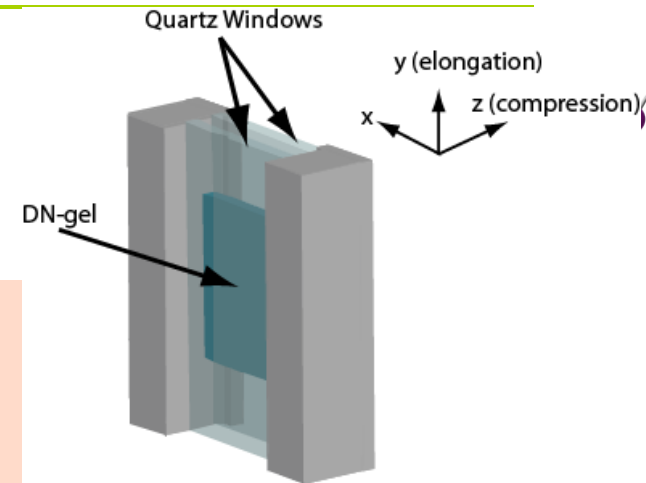

SDD ~ 8 m.

Clay-PNIPAm Nanocomposite

Side-ring gels w/ polyrotaxane

Deformation in extensible hydrogels propagates down to molecular scale.
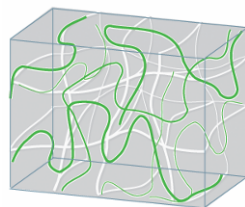
Uniaxial Extension of DN-Gel

Quartz Windows

y (elongation)

z (compression)

x

DN-gel

SDD = 4.5 m

Fracture stress / MPa

0M (SN), 0.5M, 1M, 2M, 3M, 5M

Molar ratio of 2nd to 1st network

100% uniaxial extension
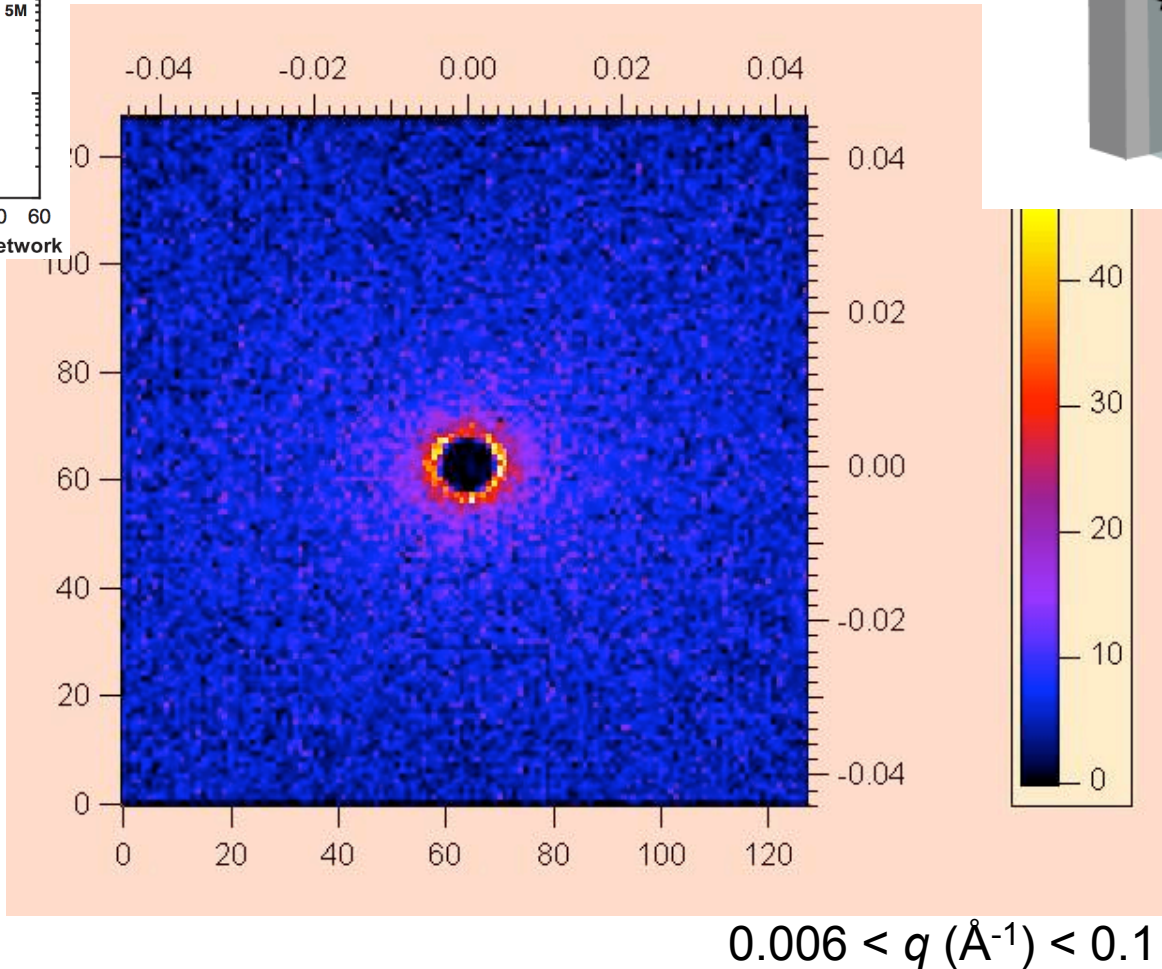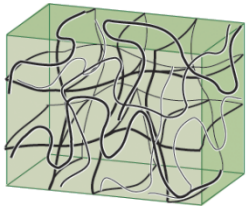
Total DN-gel:

PAMPS + PAAm

$0.006 < q$ (Å^{-1}) < 0.1

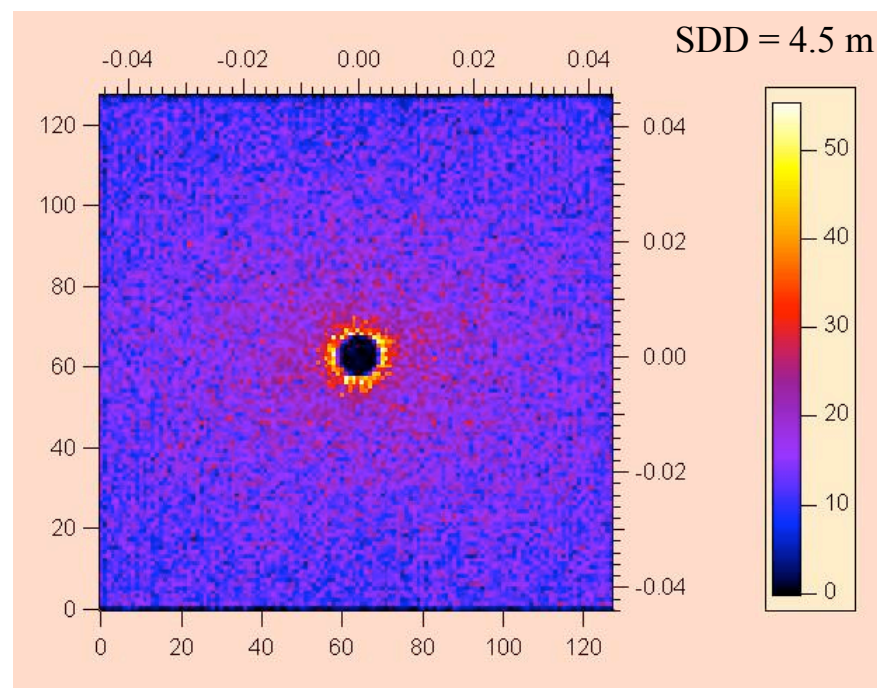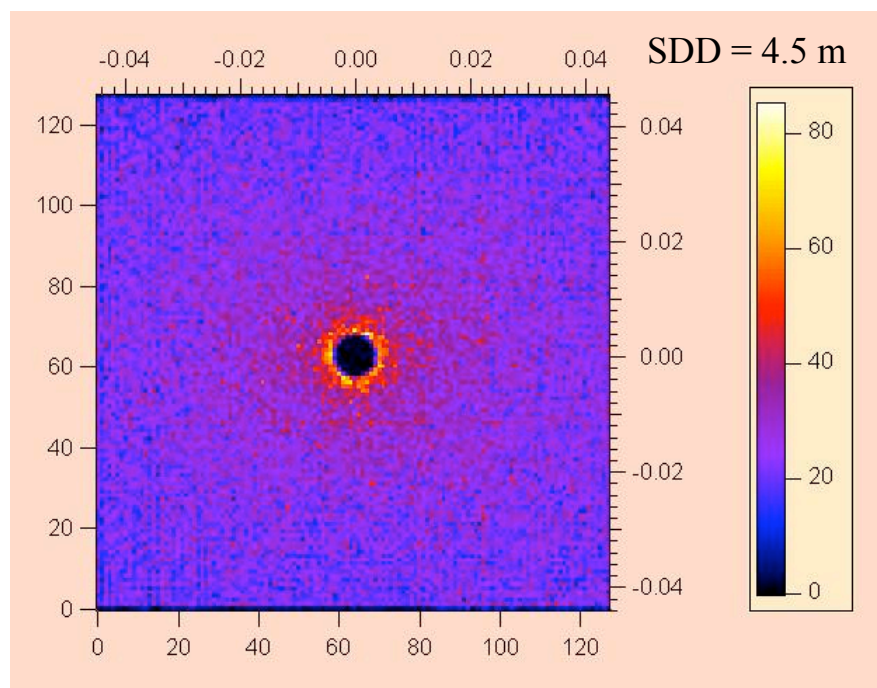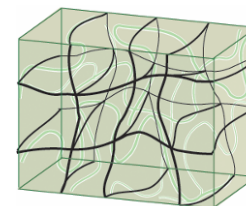**No anisotropy in small-angle scattering.**

Uniaxial Extension of DN-Gel

_d_PAAm chains in PAMPS network

Contrast-matched _d_PAAm chains in PAMPS network
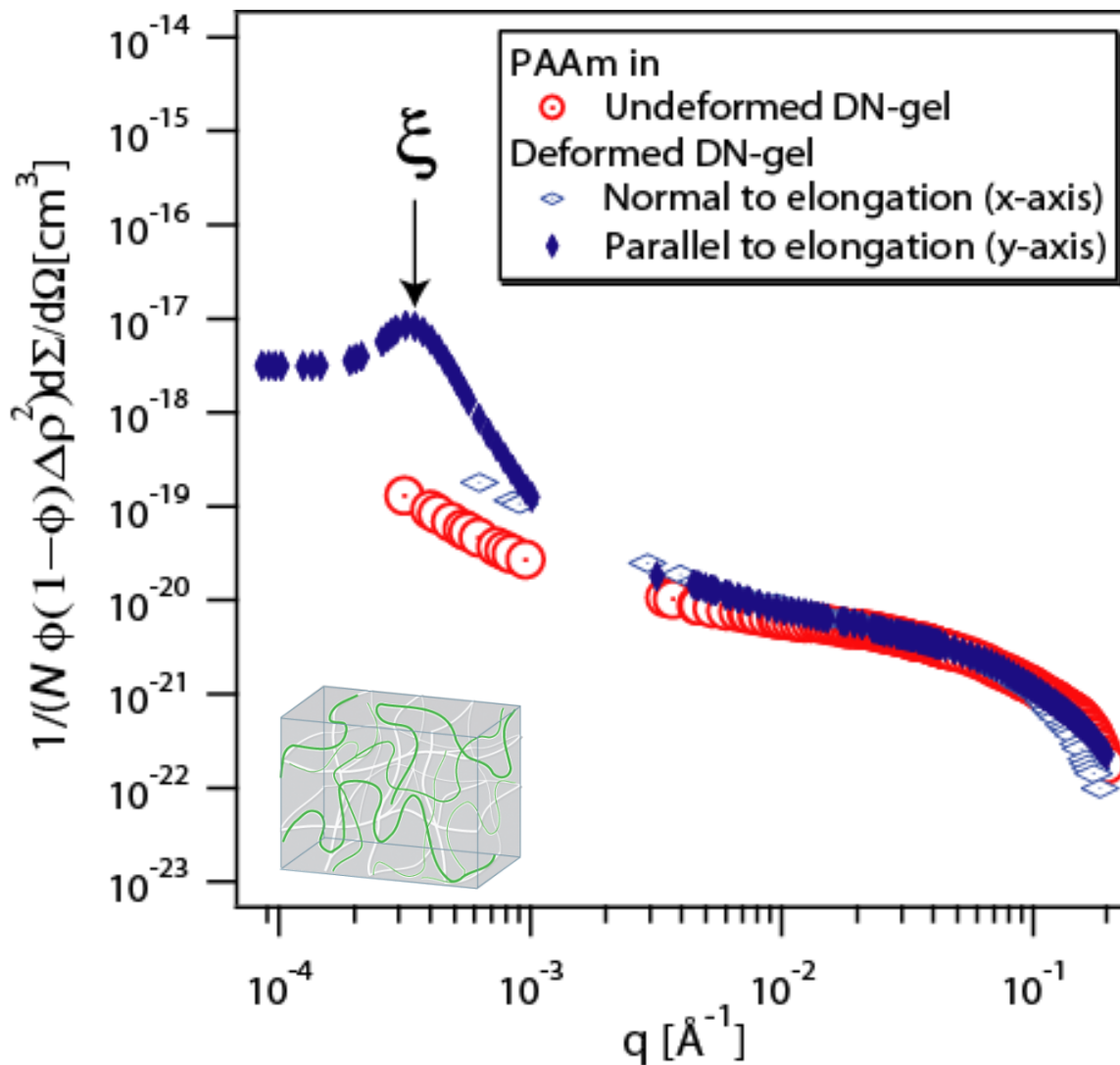
No anisotropy in the small-angle region, $0.002 \leq q$ (Å^{-1}) ≤ 0.2.

Uniaxial stress is effectively relaxed at small length scales.

Toughest DN-gel under pure shear

dPAAm chains in PAMPS network
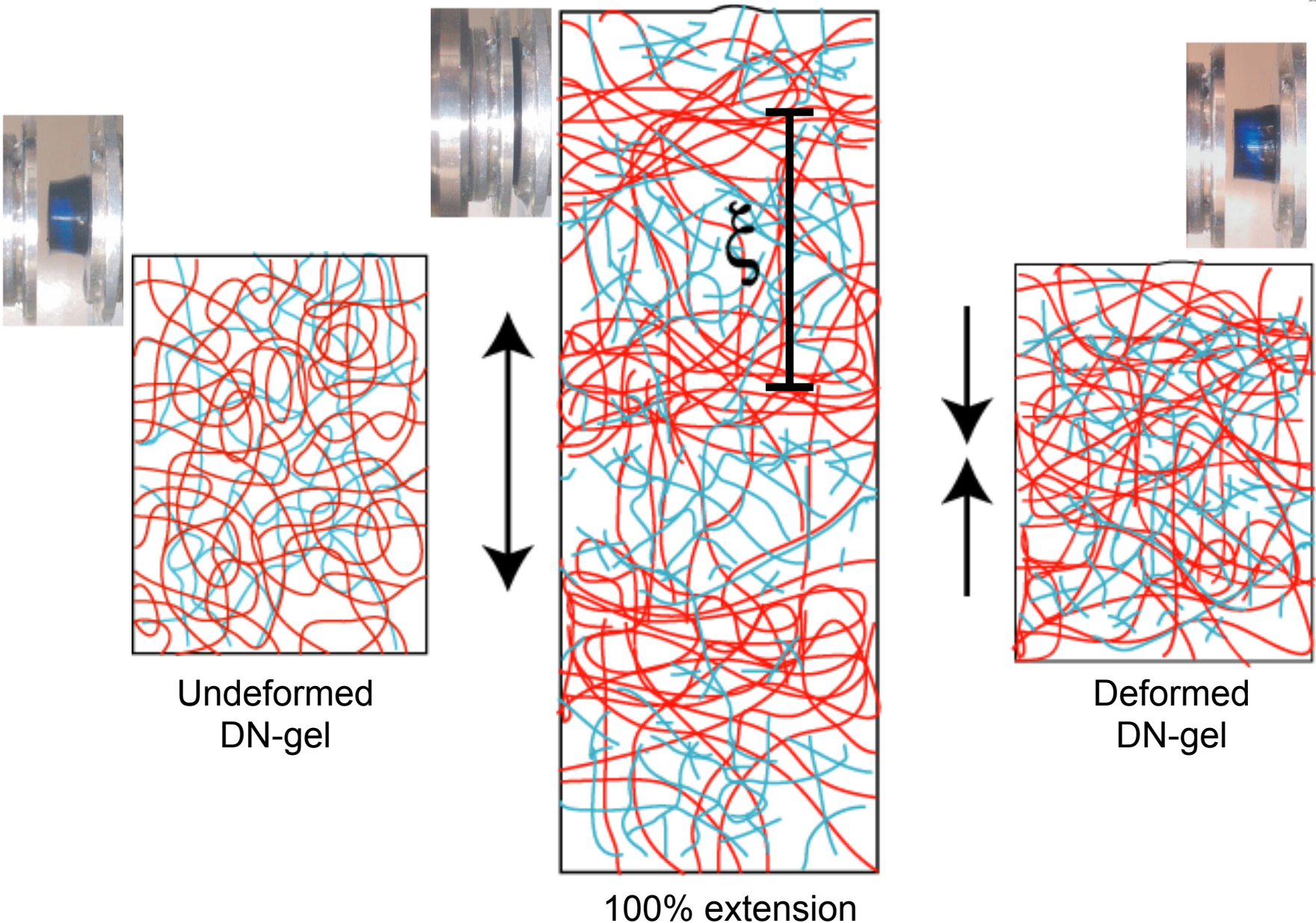

Strong low q anisotropy.

Structural Response to Deformation in DN-gels

Undeformed
DN-gel

ξ

100% extension

Deformed
DN-gel

SANS Data Anaysis: Theory

Static scattering from mixtures of polyelectrolytes and neutral chains :

Benmouna and Vilgis Macromolecues, 1991, 24, 3866.
Benmouna, Vilgis, Hakem and Negadi, 1991, 24, 6418.

$$S^{-1}(q) = S_o^{-1}(q) + V$$

$S(q)$ Total Structure Matrix $S_o(q)$ Bare Structure Matrix

V Interaction Matrix q $4\pi/\lambda(\sin\theta)$

Theoretical Model – Contd…

3-component system of **polyelectrolyte, neutral polymer and solvent**

2 X 2 Matrices are needed. (Incompressible system.)

PE : Polyelectrolyte (PAMPS), NP : Neutral Polymer (PAAm), S : Solvent (water)

$$S_o(q) = \begin{pmatrix} S_{PE}^o & 0 \\ 0 & S_{NP}^o \end{pmatrix} \qquad V = \begin{pmatrix} \upsilon_{PE-PE} & \upsilon_{PE-NP} \\ \upsilon_{PE-NP} & \upsilon_{NP-NP} \end{pmatrix}$$

$$\upsilon_{PE-PE} = \frac{1}{\varphi_S} - 2\chi_{PE-S} + \frac{4\pi l_b}{q^2 + \kappa^2}$$

$$\upsilon_{NP-NP} = \frac{1}{\varphi_S} - 2\chi_{NP-S}$$

$$\upsilon_{PE-NP} = \frac{1}{\varphi_S} - \chi_{PE-S} - \chi_{NP-S} + \chi_{PE-NP}$$

φ_S : Volume fraction of the solvent

l_b : Bjerrum length

κ^{-1} : Debye length

Theoretical Model – Contd…

$$\frac{1}{S_{AA}} = \frac{1}{S_A^o} + \upsilon_{AB} - \frac{\upsilon_{AB}^2 S_B^o}{1 + \upsilon_{BB} S_B^o}$$
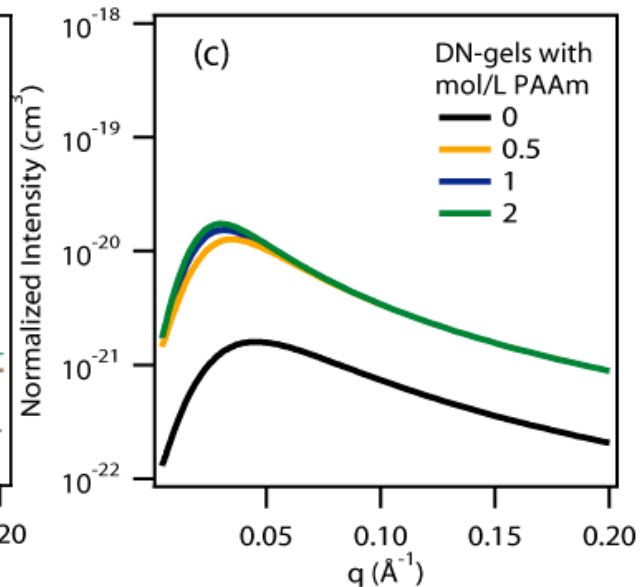
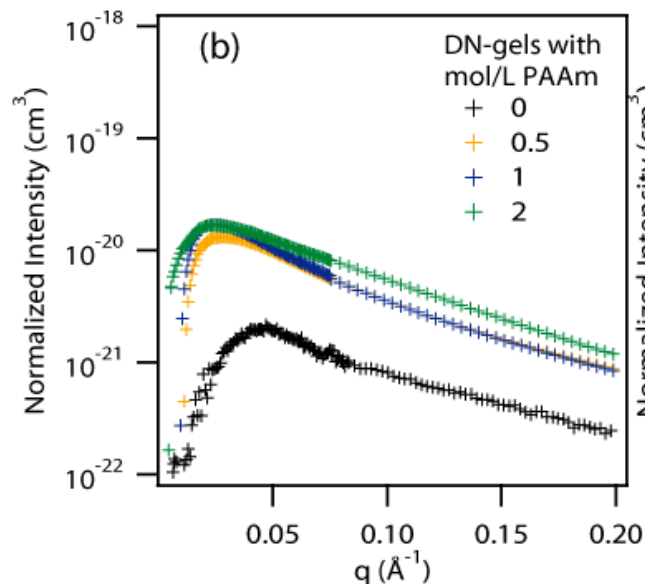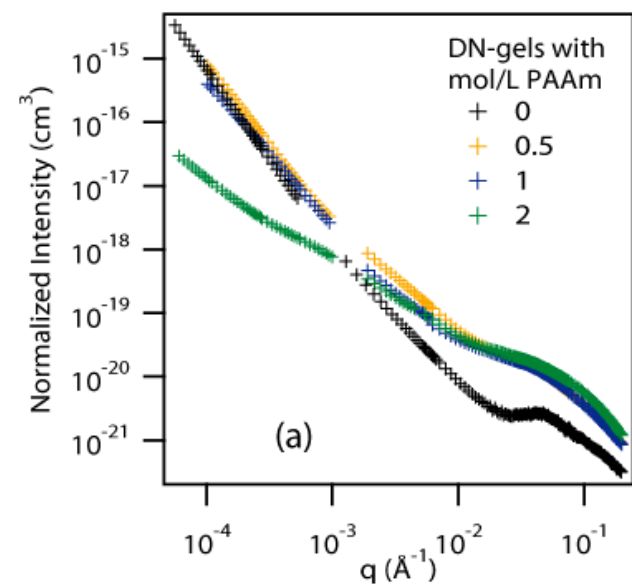$$S_A^o = \varphi_A N_A P_A(q)$$

φ_A : Volume fraction of A

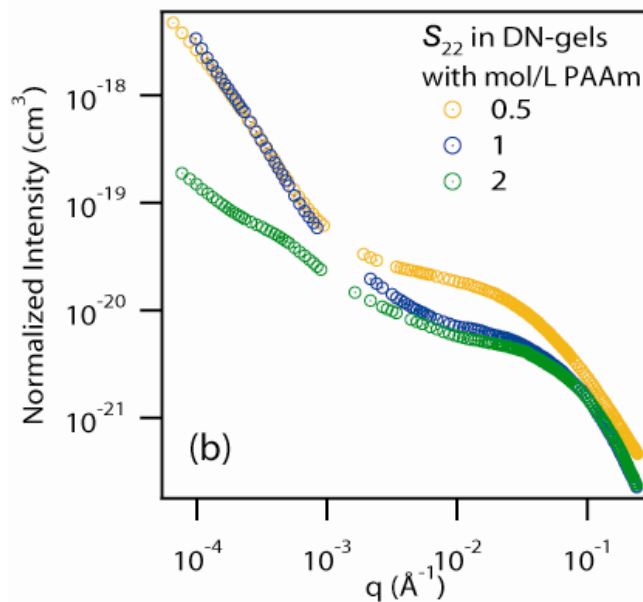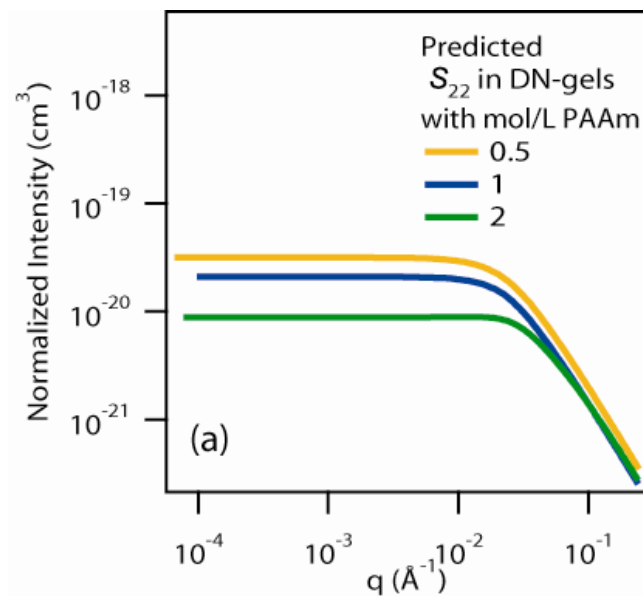N_A : Degree of polymerization of A

$P_A(q)$: Form factor of A (Debye function)

$$P_A(q) = \frac{2}{\alpha^2}\left[e^{-\alpha} + \alpha - 1\right] \qquad \alpha = q^2 R_g^2$$
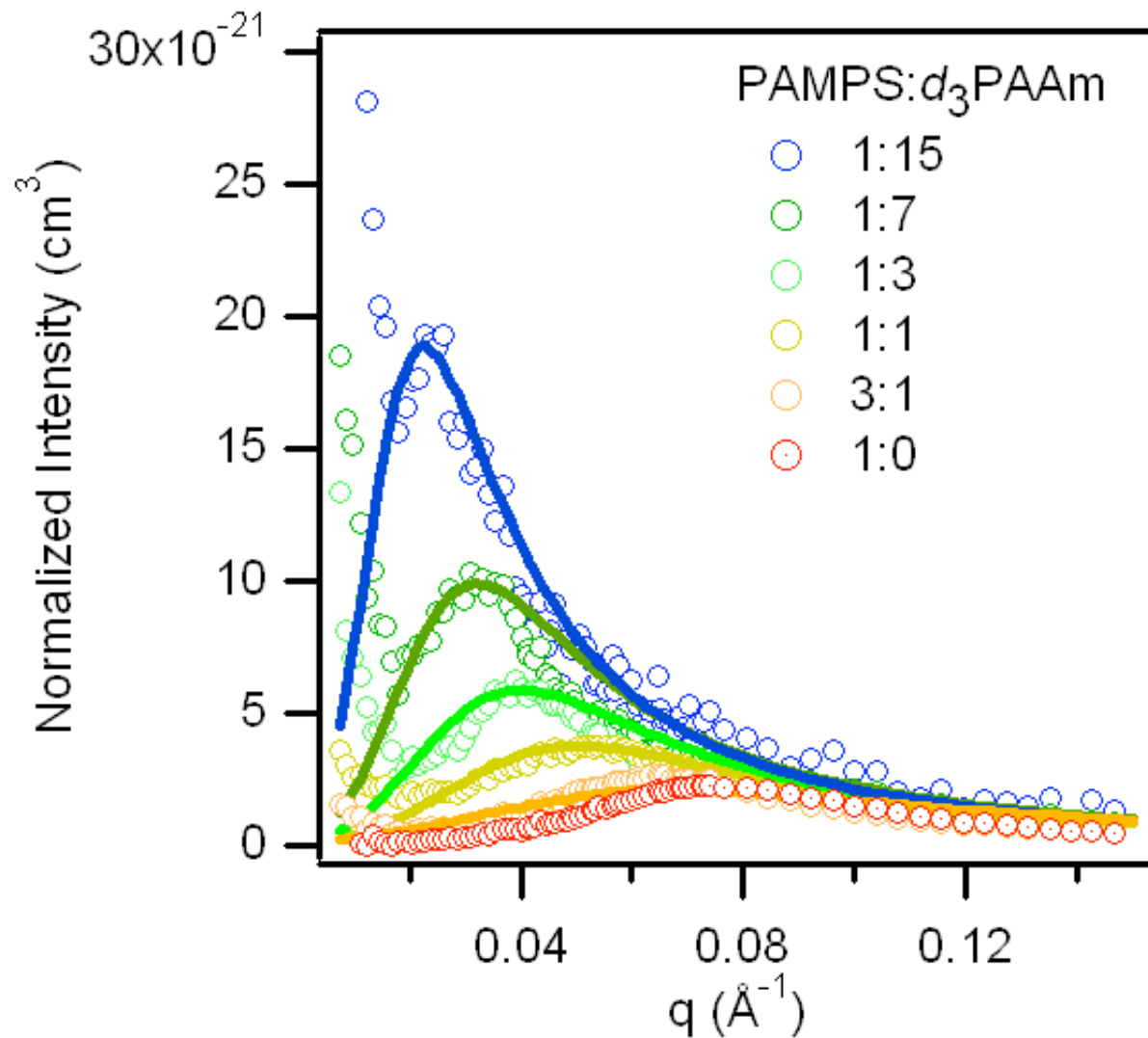
Fitting Results: PAMPS

Tominaga, Tirumala *et al. J. Phys. Chem.* **2008**.

Fitting Results: PAAm

Fitting Results: PAMPS/PAAm solution blends

Best Fit Parameters

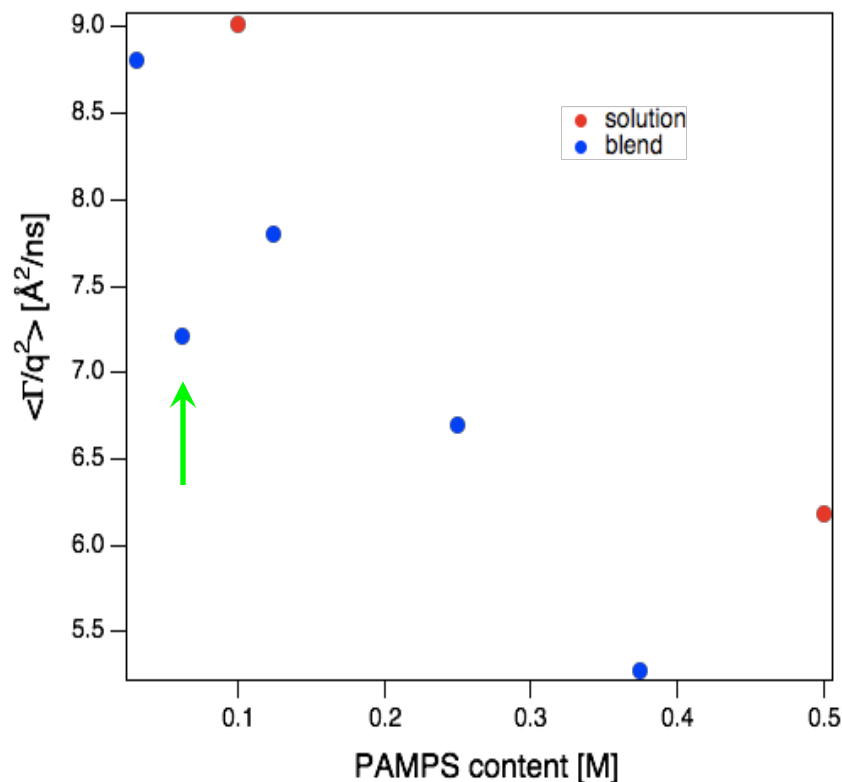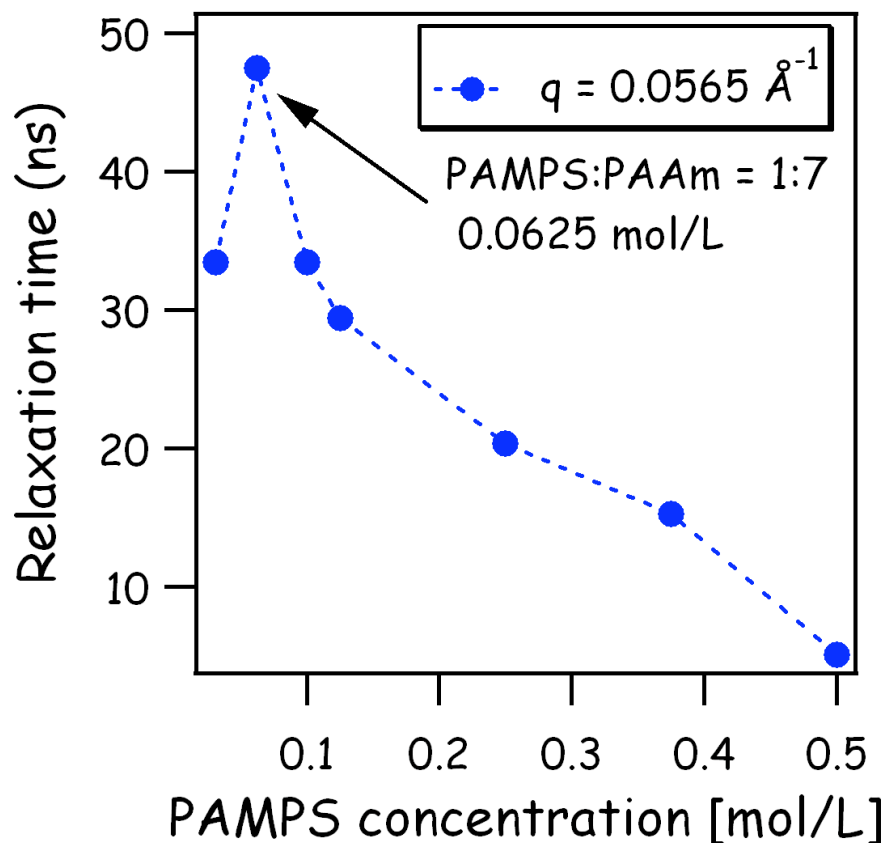|	χ_{PE-S}	χ_{NP-S}	χ_{PE-NP}	Mesh length (Å)
Pure PE (PAMPS)	0.2	-	-	140
0.5 M DN	0.2	0.45	0.03	545
1M DN	0.2	0.44	0.03	771
2M DN	0.2	0.48	0.03	860

PAMPS/PAAm Solution Blends
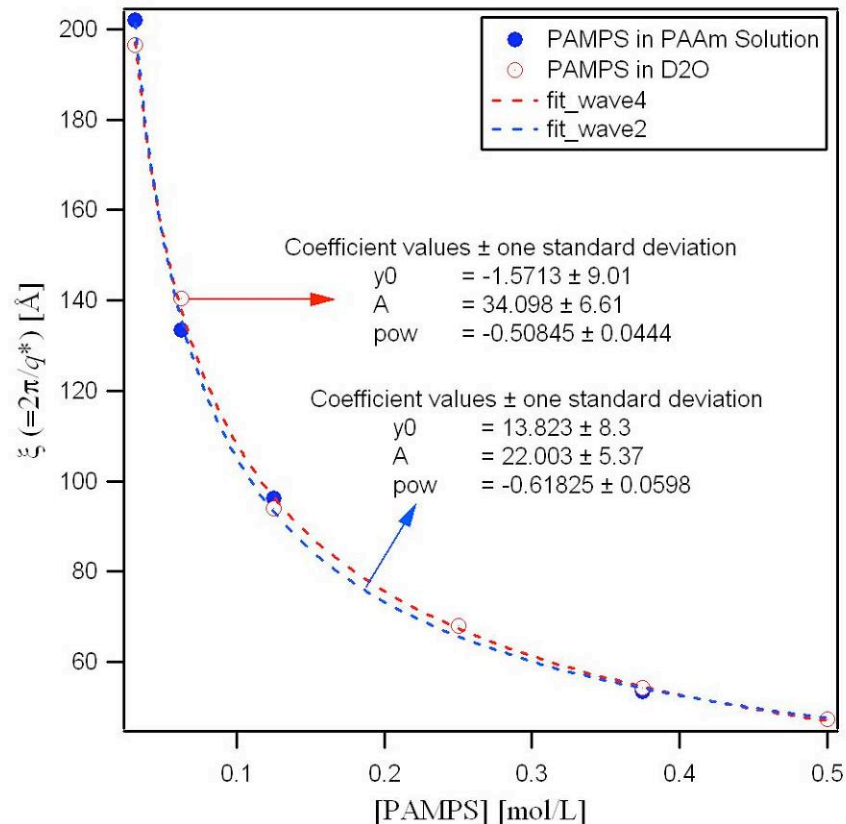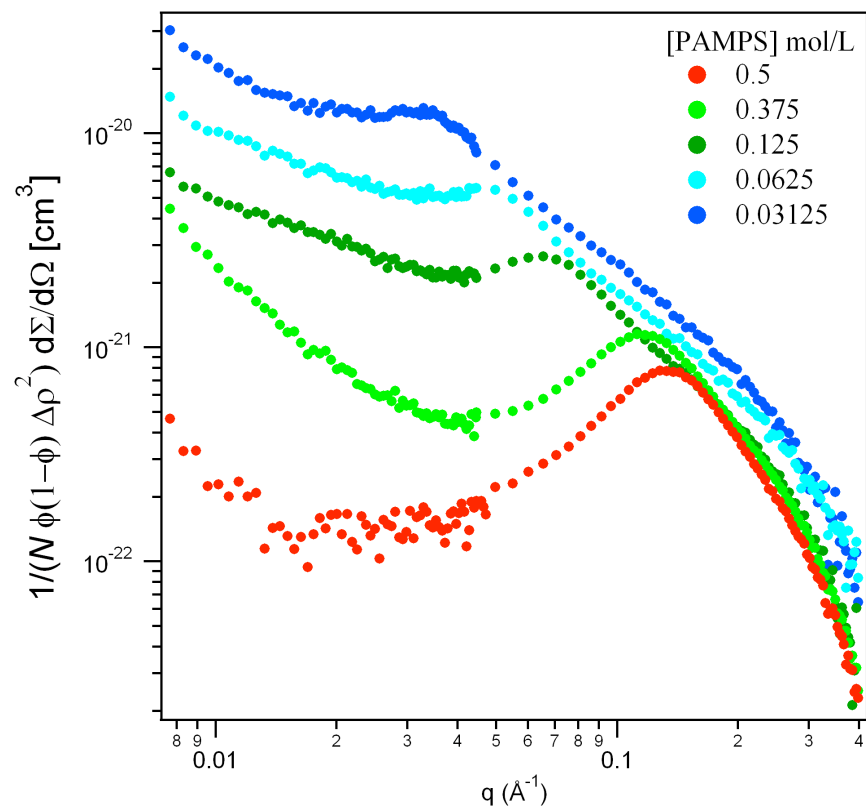
Scaling relationship: polyelectrolyte peak position, $q^* \sim [c]^{-0.5}$
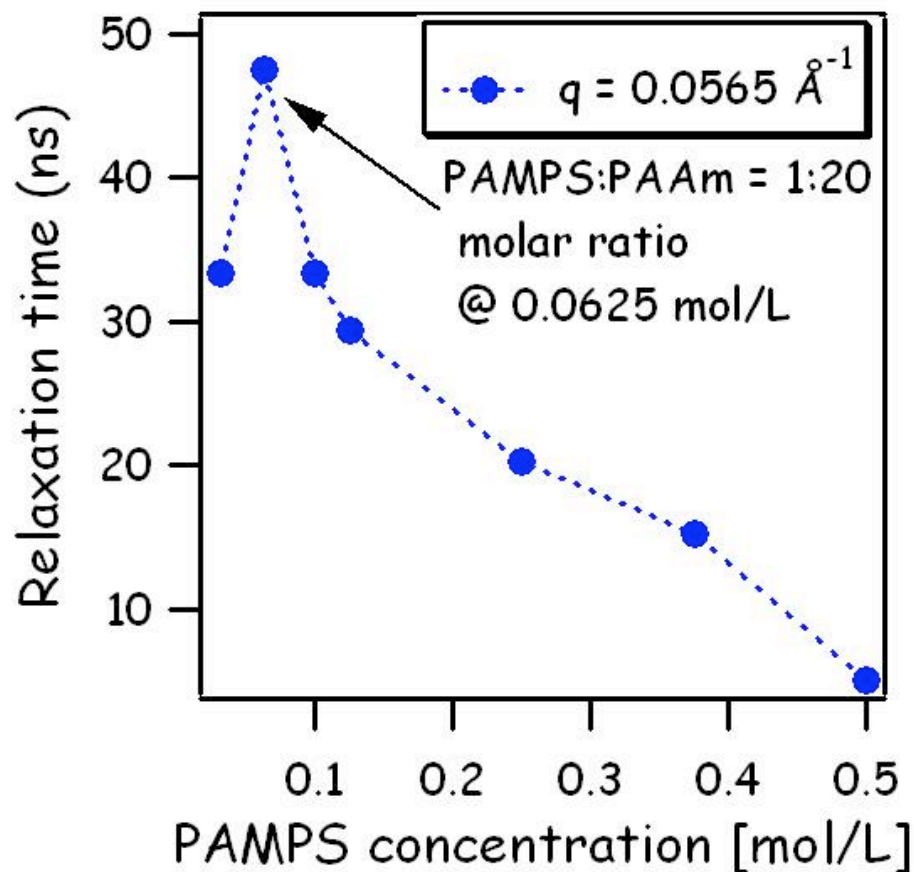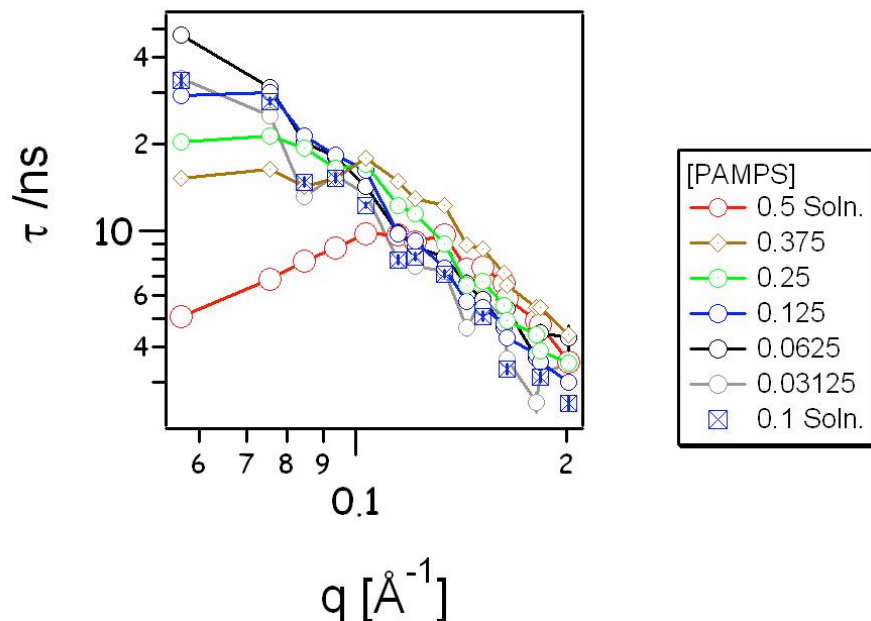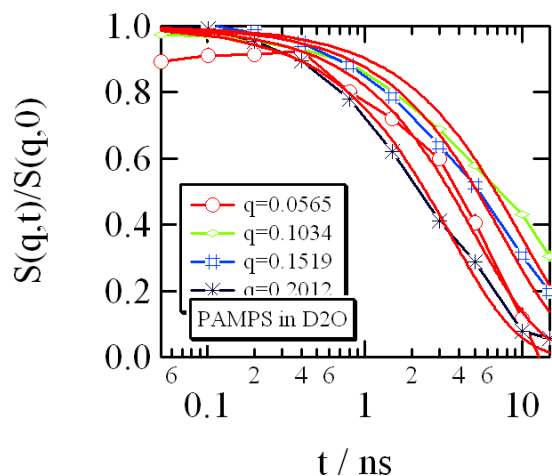
Exponent 0.6 → Excluded volume interactions

Muthukumar, *J. Chem. Phys.* **1996.**

Anomalous Fluctuations in PAMPS/PAAm Solution Mixtures: Neutron Spin-Echo
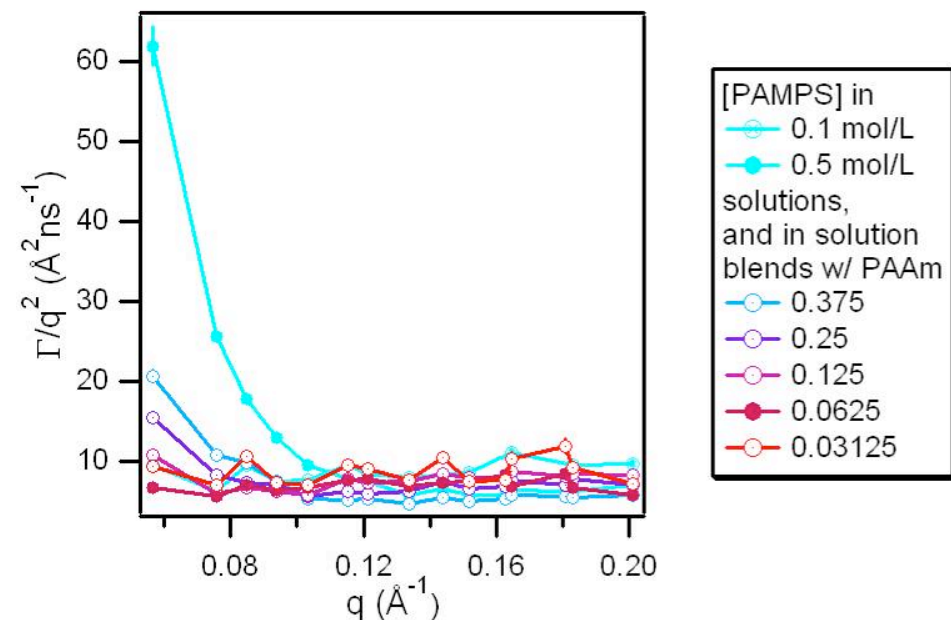
# PAMPS/PAAm Solution Blends: Neutron Spin-Echo Spectroscopy

Anomalous slowing down of PAMPS relaxation at a critical molar ratio indicates complexation.

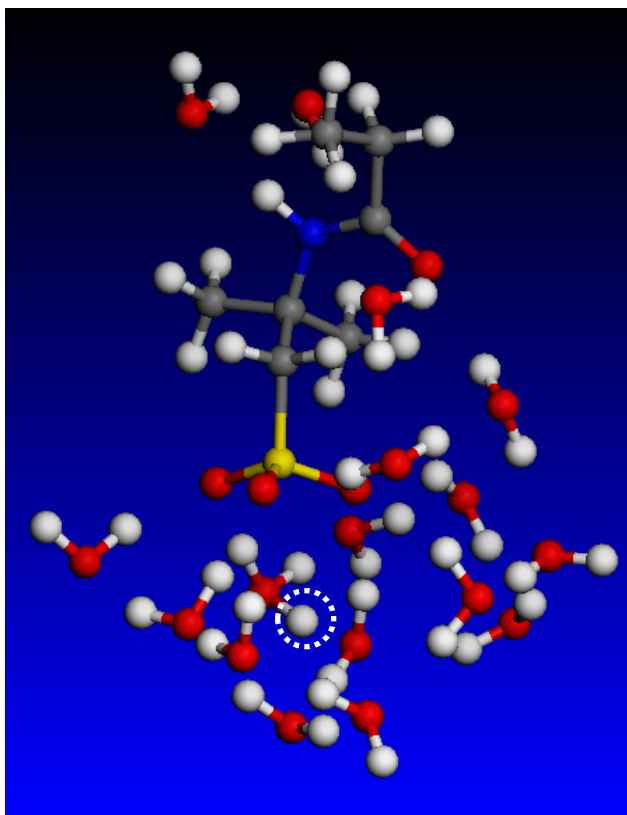# Anomalous Fluctuations in PAMPS/PAAm Solution Mixtures: Neutron Spin-Echo

Reduced diffusivity of PAMPS backbone at a critical PAMPS/PAAm molar ratio indicates complexation between the DN-gel constituents.
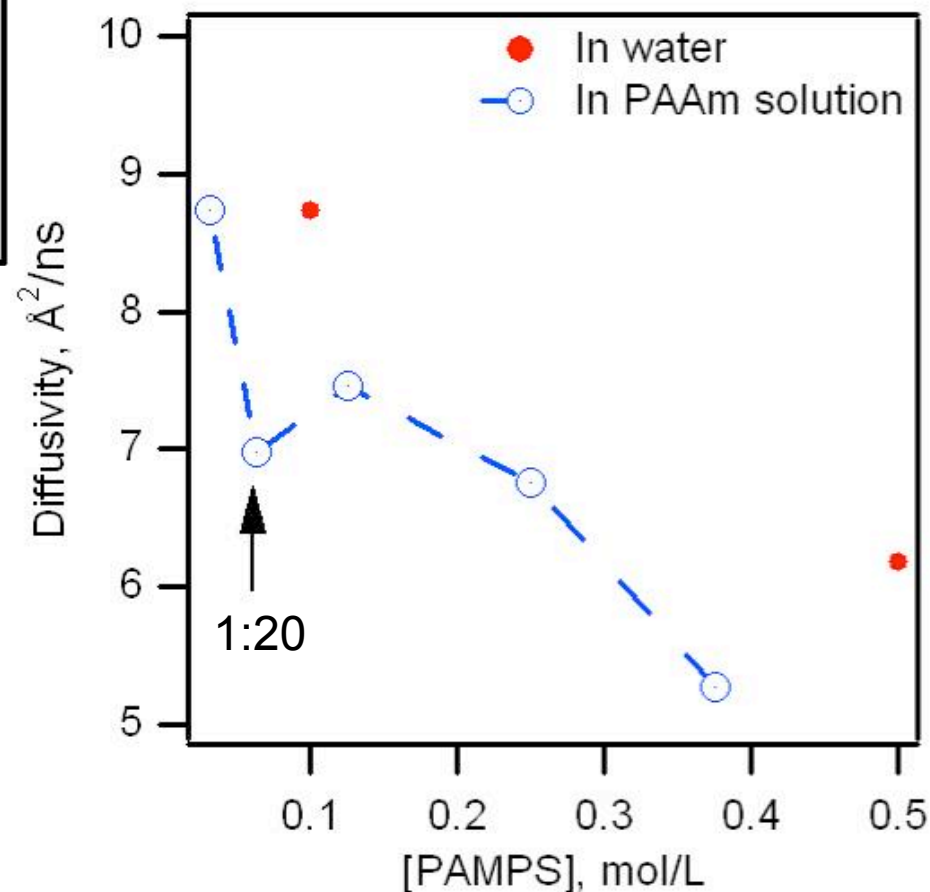
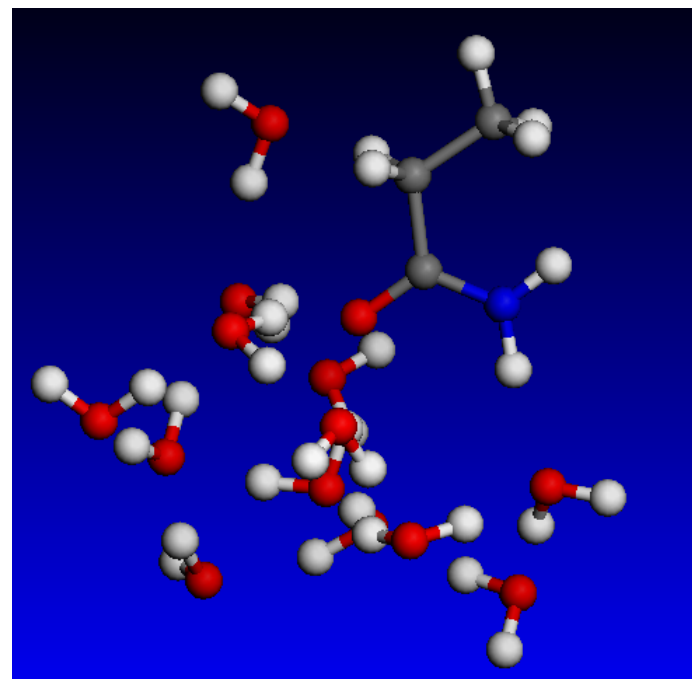# Charge Mismatch: AMPS & AAm in Water

Courtesy: Prof. Anil Kandalam, VCU Physics

AMPS in water

Atomic Charge = - 0.481 Mullikens
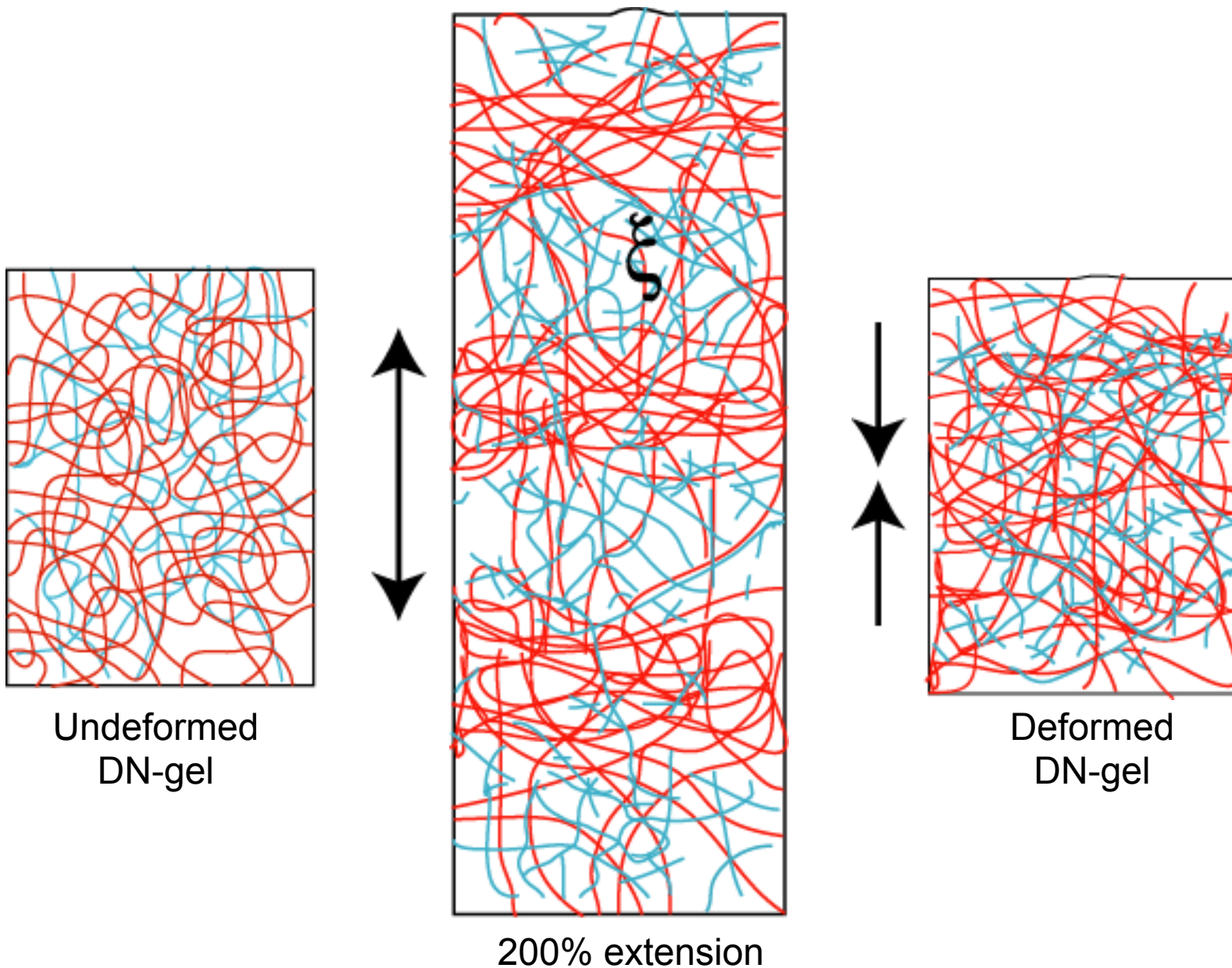
AAm in water

Atomic Charge = + 0.022 Mullikens

Ratio of accumulated charge on the monomers in water, AMPS/AAm ~ 21.86

Deformation Mechanism in DN-gels

Undeformed
DN-gel

ξ

200% extension

Deformed
DN-gel

Summary

❑ Enthalpic association between the constituents allows for energy dissipation and stress-transfer from first network to the second.

❑ PAAm linear chains undergo dynamic reorganization under an applied load.

❑Linear polyacrylamide chains *reinforce* the DN-gels to sustain large deformations.

Conclusion
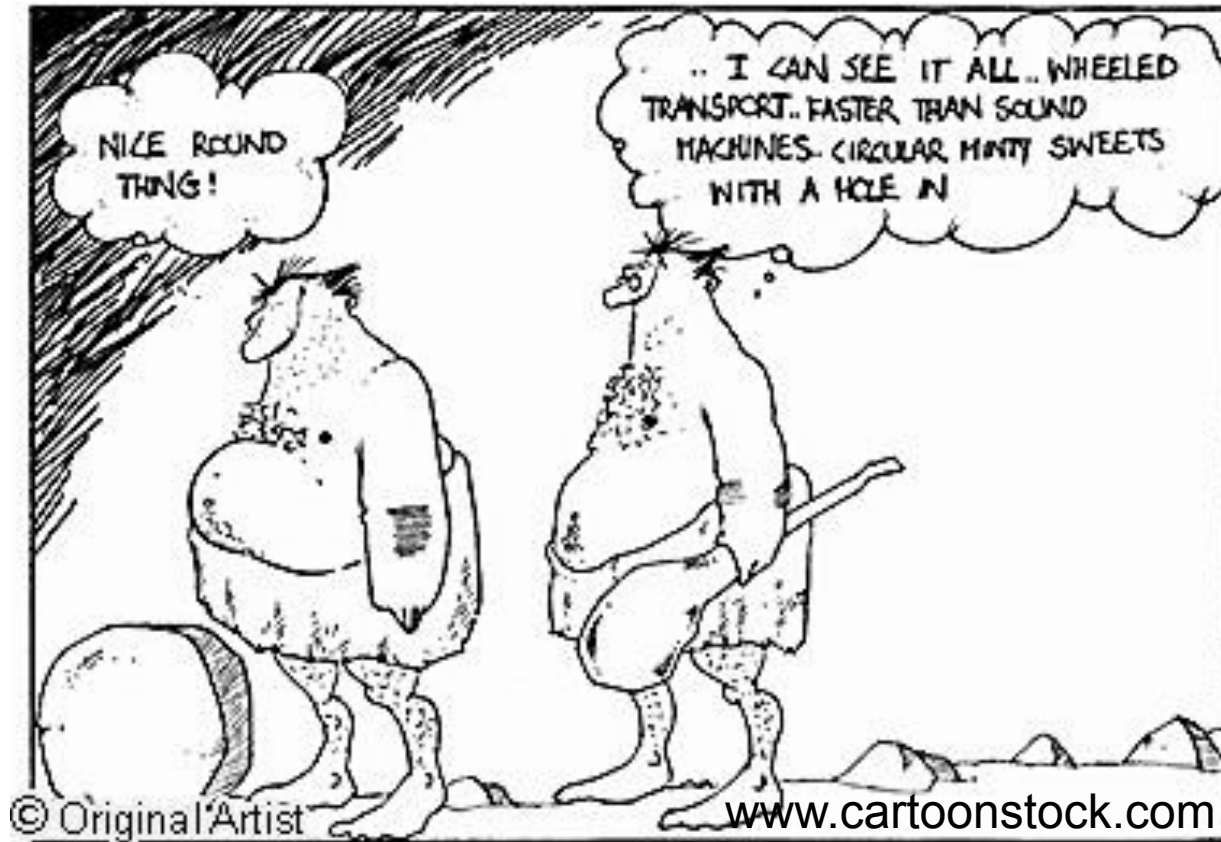
Understanding from the studies of blend systems can be readily applied to problems in polymer nanocomposites.

polymer-particle interactions affect dispersion & performance.

Eg. well dispersed carbon black fillers improve elastomer properties.

Thanks to…

Jeff Kryzwon, Bryan Greenwald, Dr. John Barker

If I could solve all the problems myself, I would. – *Thomas Edison*